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NOVEL RING OPENING REACTION OF 2,3-DIPHENYL AND 2,3-DI-n-PROPYL-CYCLOPROPENYLIDENEANTHRONE

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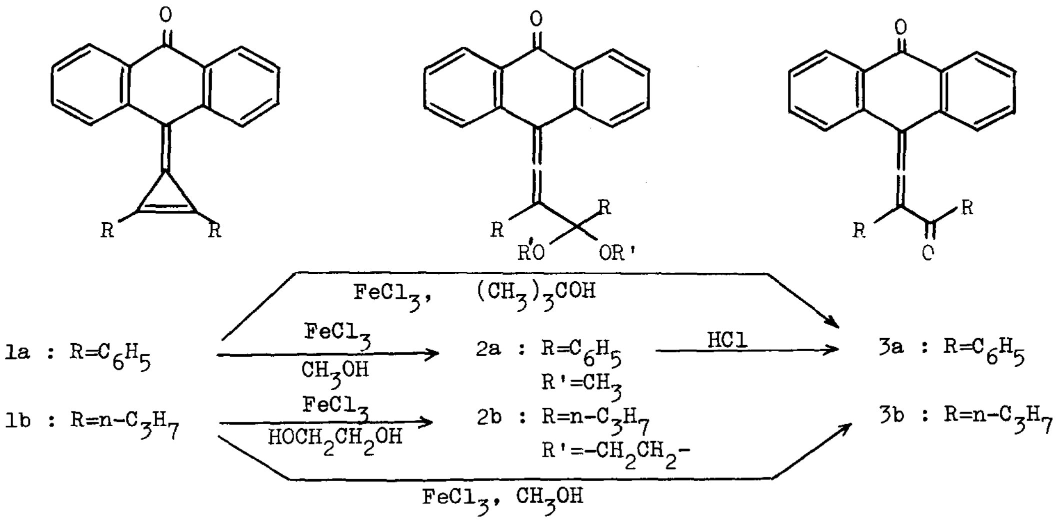
The chemistry of cyclopropenylideneanthrones 1) has considerable significance owing to the contribution of the dipolar resonance form to the ground state of these molecules. Although the ring opening and the ring enlargement reactions of the three-membered ring in the cyclopropenylidenecyclopentadiene (calicene) system by the various cycloaddition reactions have been extensively investigated 2) there appears to be no information about the chemical properties of the cyclopropenylideneanthrone.

We now report novel ring opening reactions of 10-[2,3-diphenylcyclopropenylidene]anthrone (1a) 1) and 10-[2,3-di-n-propylcyclopropenylidene]anthrone (1b) 1) by alcoholysis in the presence of ferric chloride in which the type of products depends on the substituents of the cyclopropene ring and the alcohol.

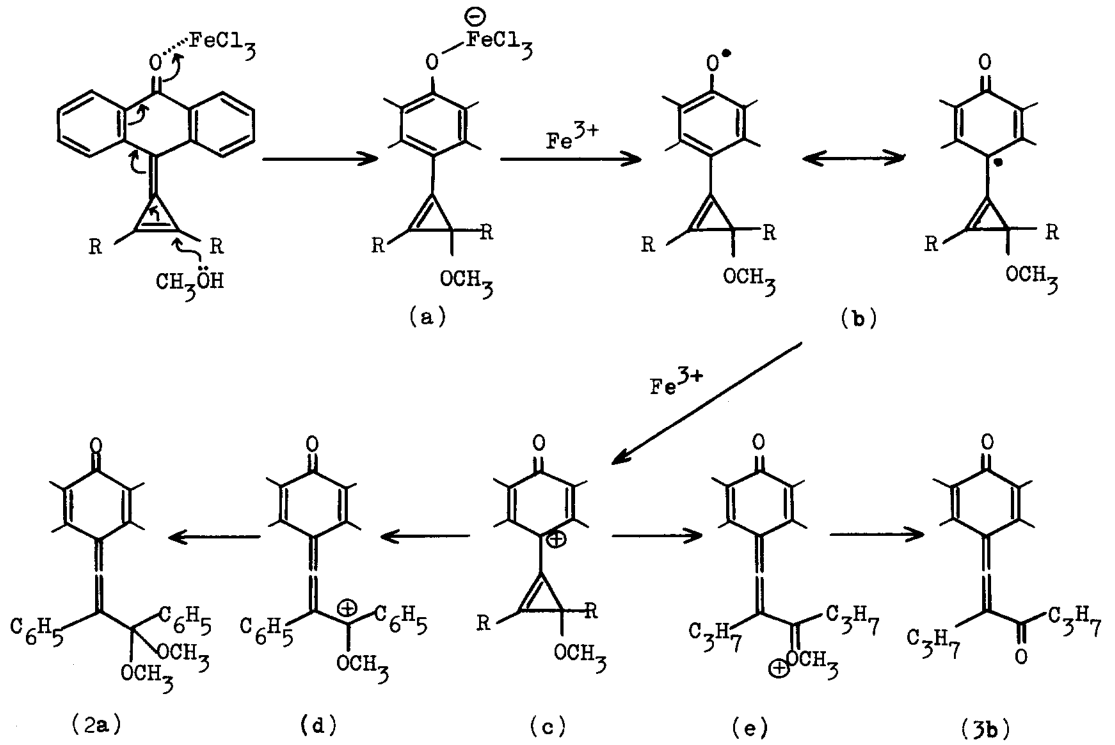
A reaction of (1a) [scheme-1] with ferric chloride in absolute methanol under nitrogen gave (2a), colorless prisms, m.p. 204-205°C (decomp) in 90.2 % yield. The elemental analysis [Found: C, 84.01; H, 5.46 %, Calcd. for $C_{31}H_{24}O_3$: C, 83.76; H, 5.44 %] and the spectroscopic properties [see Table-1] are in accord with the assigned structure, 10-[3,3-dimethoxy-2,3-diphenylpropenylidene-1]-anthrone. Hydrolysis of (2a) with hydrochloric acid in dioxane proceeded smoothly to give a quantitative yield of the allenic ketone (3a), pale yellow prisms, m.p. 199.5-200.5°C (decomp) [Found: C, 87.58; H, 4.59, Calcd. for $C_{29}H_{18}O_2$: C, 87.41; H, 4.55 %].



Scheme-1

Table-1. Spectral Data of 2a, 2b, 3a and 3b

	$\lambda_{max}^{CH_3CN}$ (n.m)	log ε	ν_{max}^{KBr} (cm^{-1})		proton assignment		δ (ppm)	
2a	236	4.65	1915	(C=C=C)	OCH_3	(6H)	3.30	s
	282	4.33	1650	(arom. C=O)	peri-H	(2H)	8.48	d.d
	347	4.09	1600	(arom.)	aromatic	(16H)	7.1-8.1	m
	361	4.16	1060,1107	(C-O-C)				
2b	237	4.64	1920	(C=C=C)	$-O-CH_2CH_2-O-$	(4H)	4.00	s
	275	4.28	1640	(arom. C=O)	peri-H	(2H)	8.50	d.d
	351(s)	4.06	1590	(arom.)	aromatic	(6H)	7.3-8.0	m
	364	4.20	1059	(C-O-C)	CH_3	(6H)	0.90	t
					CH_2	(8H)	1.2-2.5	m
3a	235	4.70	1898	(C=C=C)	peri-H	(2H)	8.47	d.d
	252	4.46	1650	(arom. C=O, C=O)	aromatic	(16H)	7.3-8.3	m
	284	4.36	1598	(arom.)				
	364	4.11						
3b	236	4.71	1919	(C=C=C)	CH_3	(3H)	0.83	t
	248	4.21	1683	(C=O)	CH_3	(3H)	1.23	t
	289	4.28	1653	(arom. C=O)	$CO-CH_2-$	(2H)	2.90	t
	361	4.12	1600	(arom.)	$=C-CH_2-$	(2H)	2.17	t
					$-CH_2-$	(4H)	1.2-2.2	m
					peri-H	(2H)	8.43	d.d
					aromatic	(6H)	7.2-7.7	m



Scheme-2

In contrast to the above observations, di-n-propyl derivative (1b) gave the other allenic ketone (3b), colorless prisms, m.p. 110-111.5°C [Found: C, 83.34;H, 6.71. Calcd. for $C_{23}H_{22}O_2$: C, 83.60, H, 6.71%] in 83% yield, on same reaction condition as in the case of 1a. The structure of (3b) was also confirmed by the spectral evidences [Table-1].

The foregoing results suggest that the formation of allenic derivatives (2a) and (3b) are assisted by participation of ferric chloride, with the attack of methanol used as solvent possibly being initiated by association of the carbonyl group with the ferric chloride as a Lewis acid. Oxidation of the resulting anthroxide (a) by ferric ion leads, via the resonance stabilized anthroxy radical (b), to the intermediate carbonium ion (c).

In the case of a diphenyl substituted derivative (1a), the carbonium ion (c) would lead to a allenic carbonium ion (d), stabilized mainly by the resonance effect of the phenyl group, which would react with an alcohol to give the allenic ketal (2a). Alternatively, di-n-propyl cation (e) would yield the allenic ketone (3b) because most of the stabilization is expected to be achieved by delocalization of the positive charge to oxygen.

Since the reaction of (1a) with ferric chloride in t-butanol afforded exclusively (3a) whereas the di-n-propyl derivative (1b) led quantitatively to the allenic ketone ethylene ketal (2b), m.p. 112-113°C [Found: C, 80.22; H, 7.00. Calcd, for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00 %] in ethylene glycol, the difference in the formation of these products may presumably be interpreted by the steric reason.

A full account of these investigations including results obtained from the reactions of 10-[cycloheptatrienylidene]anthrone and 10-[2,6-diphenyl-4H-pyranylidene-4]anthrone will be the subject of a full paper.

REFERENCES AND FOOTNOTES

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B. Föhlisch, P. Bürgle und D. Krockenberger, Chem. Ber., **101**, 4004 (1968).

(2) H. Prinzbach and U. Fischer, Helv. Chim. Acta, **50**, 1669, 1692 (1967) and references cited therein.

(3) Recently an example of the formation of allenic acetals from the reaction between ethoxyacetylenes and 5,5-dimethyl-N-nitrosooxazolidone in glyme with lithium ethoxideethanolate has been reported.
M. S. Newman and C. D. Beard, J. Org. Chem., **35**, 2412 (1970); These authors suggested the formation through the methylenecyclopropene intermediate as one of the plausible mechanisms.